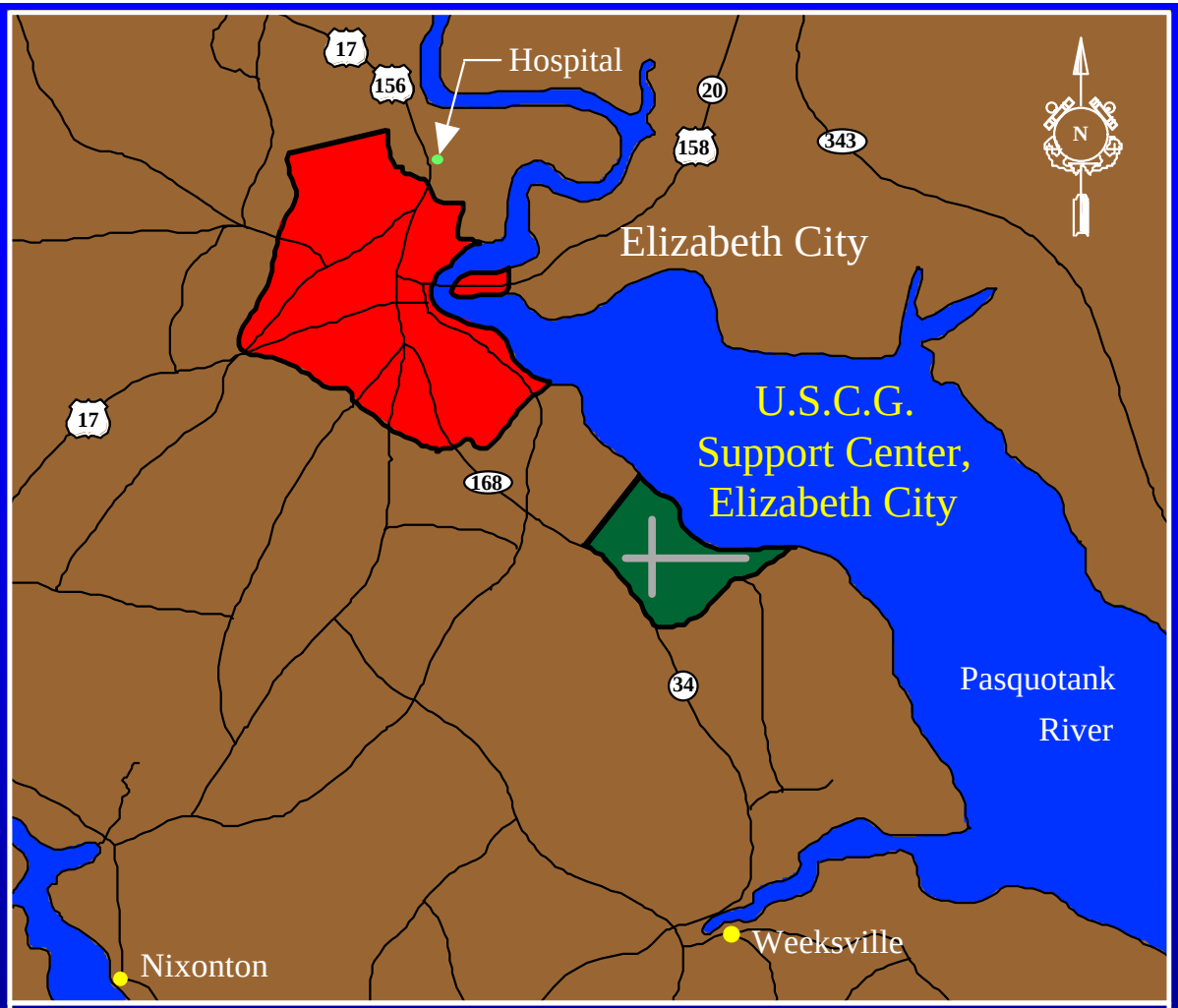
In-Situ Remediation of Chromium-Contaminated Soils and Sediments Using Sodium Dithionite

Cynthia J. Paul, Faruque, A. Khan, and Robert W. Puls

United States Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory

Ada, OK

SITE DESCRIPTION

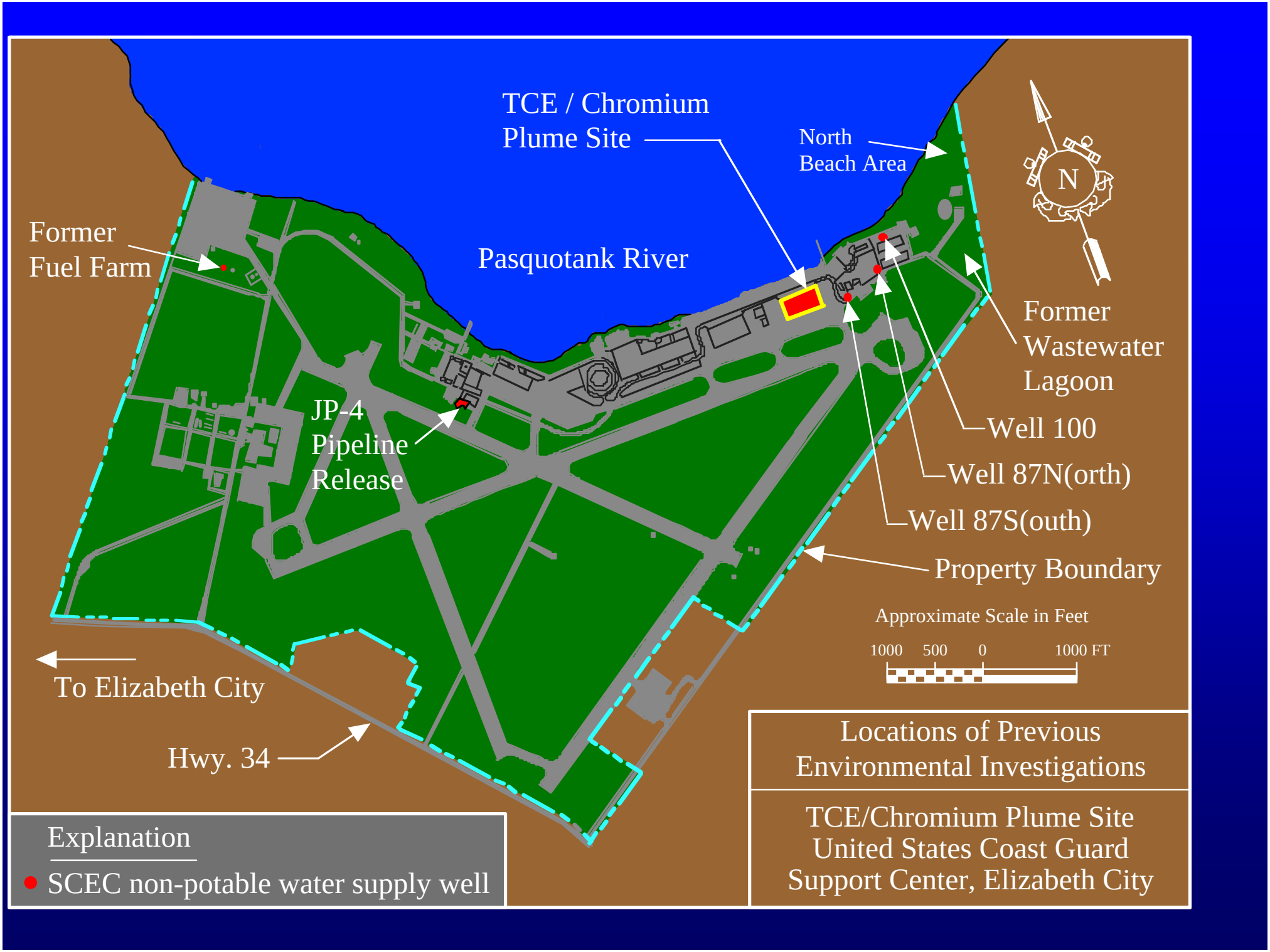


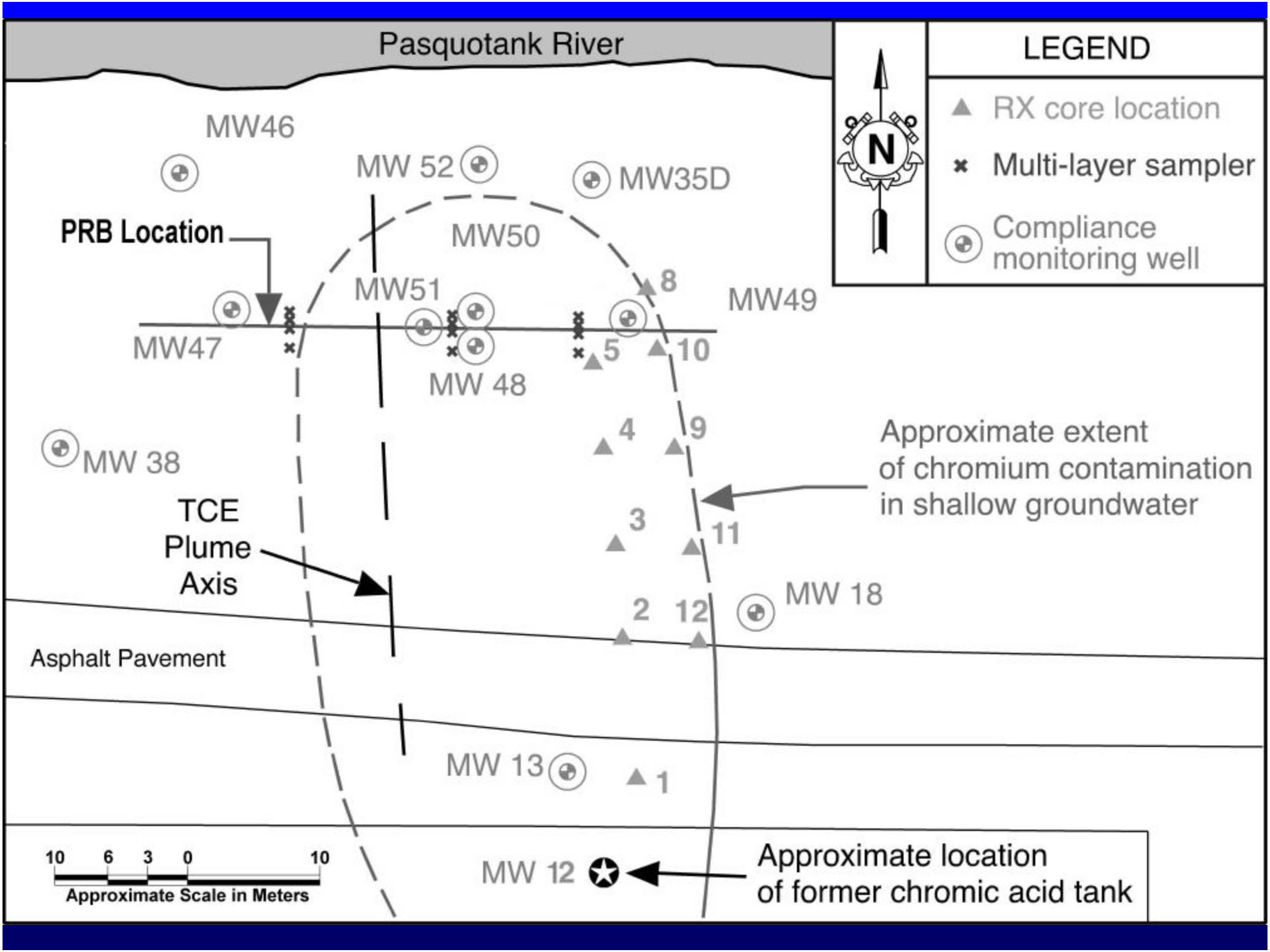
STATUTE MILES

0 1 2 3 4

Vicinity Map

TCE / Chromium Plume Site
United States Coast Guard
Support Center, Elizabeth City


TCE / Chromium
Plume Site
North
Beach Area
N
Former
Fuel Farm
Pasquotank River
Former
Wastewater
Lagoon
JP-4
Pipeline
Release
Well 100
Well 87N(orth)
Well 87S(outh)
Property Boundary
Approximate Scale in Feet
1000 500 0 1000 FT
To Elizabeth City
Hwy. 34
Explanation
SCEC non-potable water supply well
Locations of Previous
Environmental Investigations
TCE/Chromium Plume Site
United States Coast Guard
Support Center, Elizabeth City

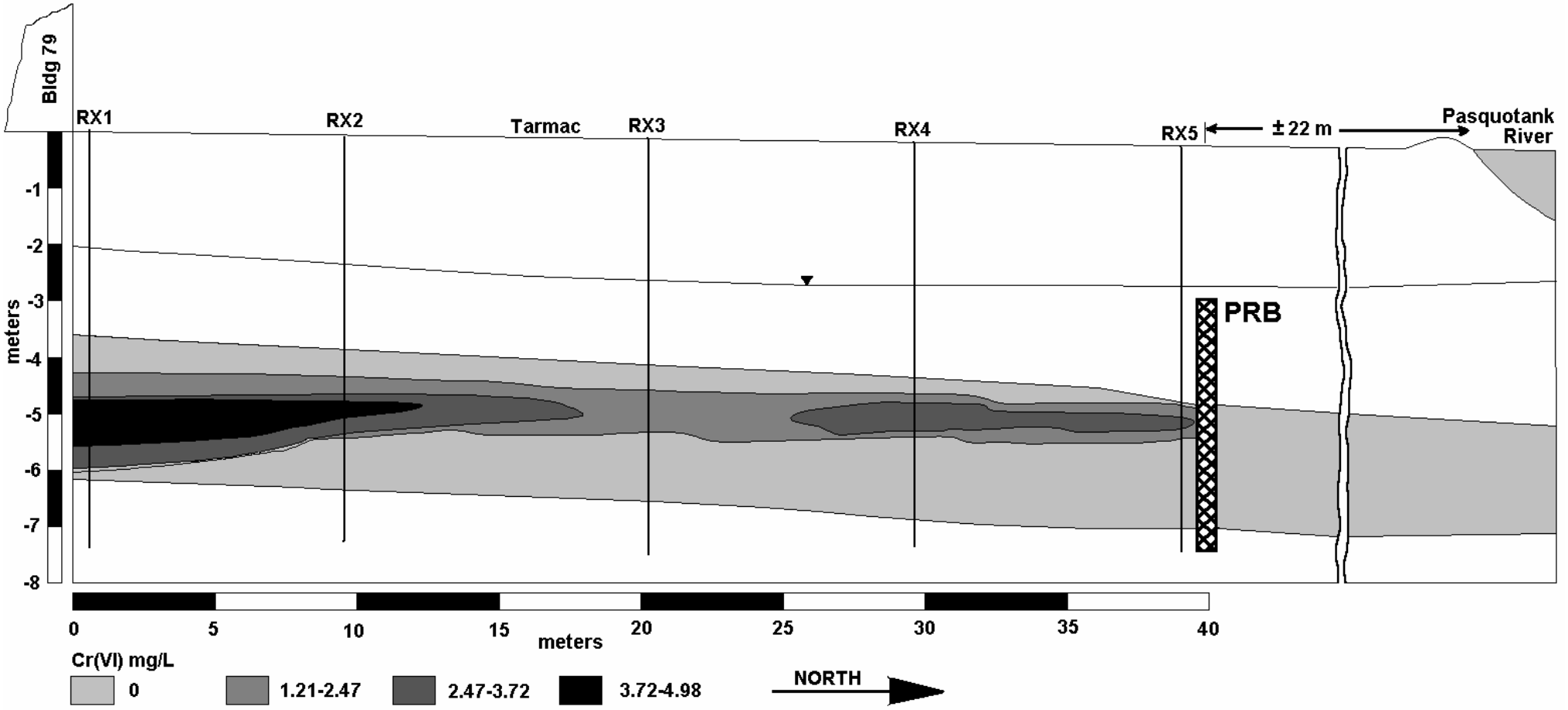

Pasquotank River
LEGEND
RX core location
Multi-layer sampler
Compliance monitoring well
N
MW46
MW 52
MW35D
MW50
PRB Location
MW51
MW49
MW47
MW 48
MW 38
TCE Plume Axis
Approximate extent of chromium contamination in shallow groundwater
MW 18
Asphalt Pavement
MW 13
MW 12
Approximate location of former chromic acid tank
10 6 3 0 10
Approximate Scale in Meters

Historical Cr(VI) Values (mg/L) in Ground Water Beneath Shop in MW 12

Feb. 1991	April 1992	June 1993	June 1994	May 1995	June 1997	June 1998	June 1999
1.60	0.80	1.41	28.0	27.0	4.40	3.00	4.25

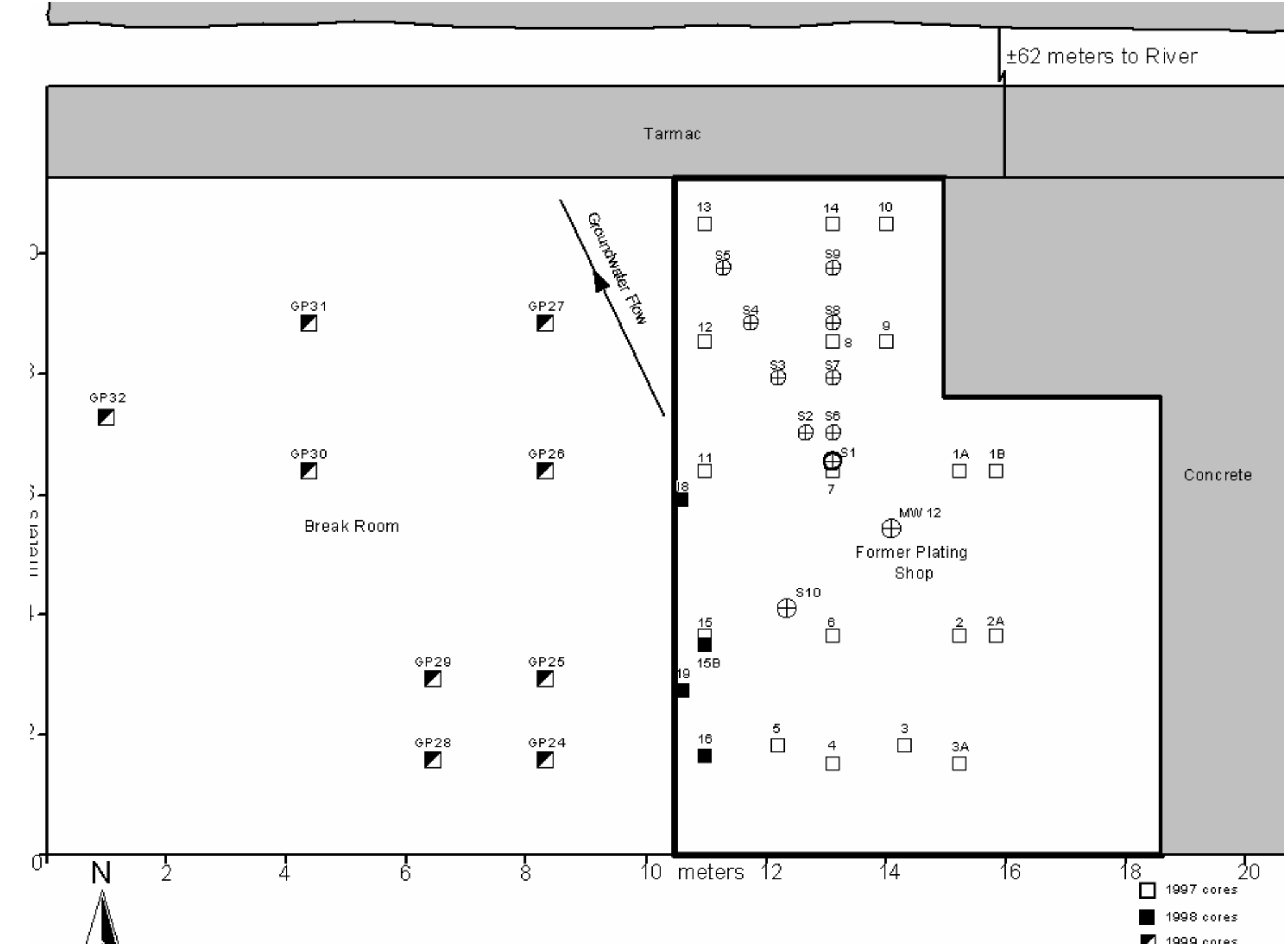
OBJECTIVES

- **Site Re-Characterization**
- **Laboratory Studies**
- **Field-Scale Pilot Study**

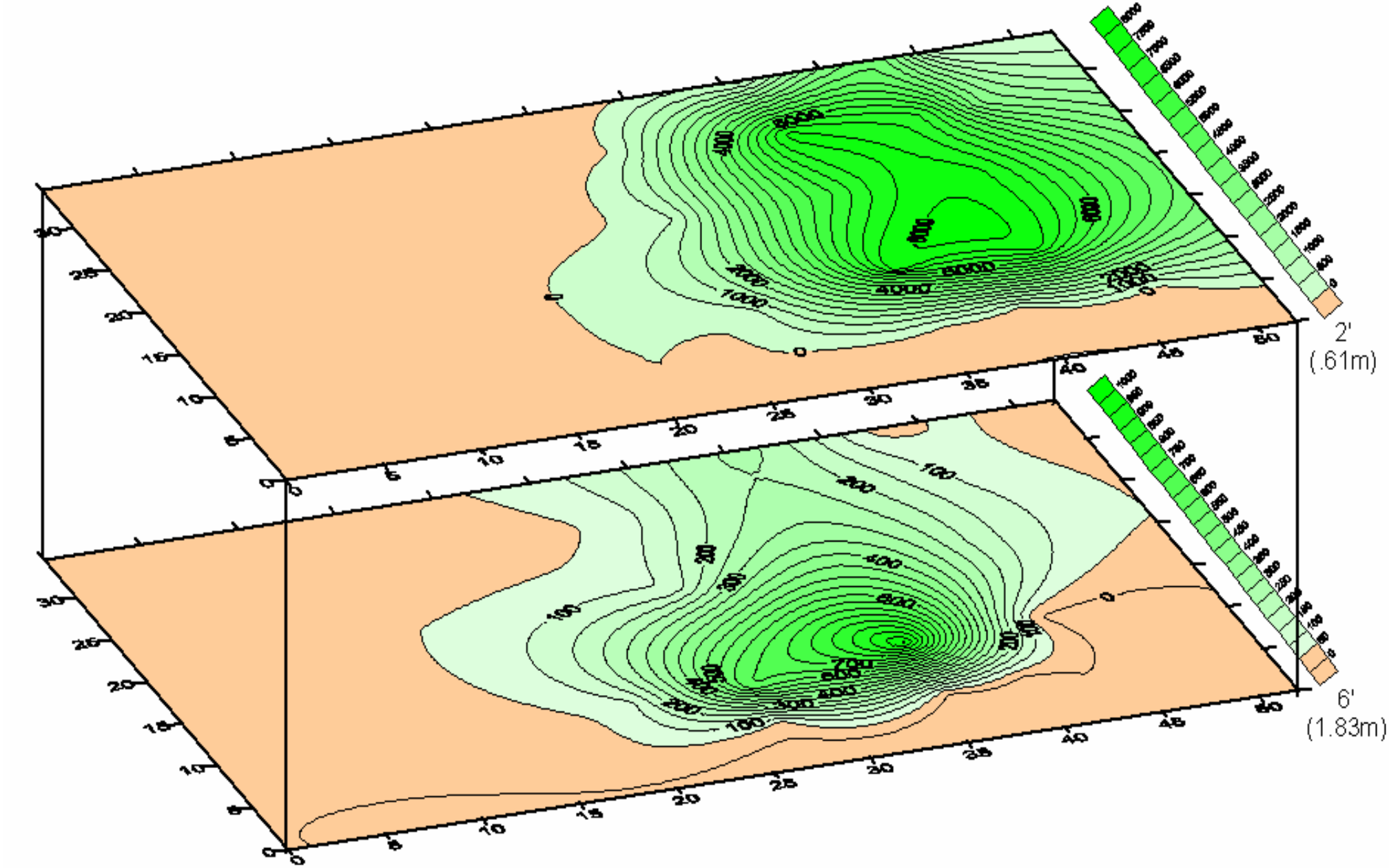

Bldg 79
RX1
RX2
Tarmac
RX3
RX4
RX5
± 22 m
Pasquotank River
PRB
meters
-1
-2
-3
-4
-5
-6
-7
-8
0
5
10
15
20
25
30
35
40
meters
Cr(VI) mg/L
0
1.21-2.47
2.47-3.72
3.72-4.98
NORTH

Soil Core Collection

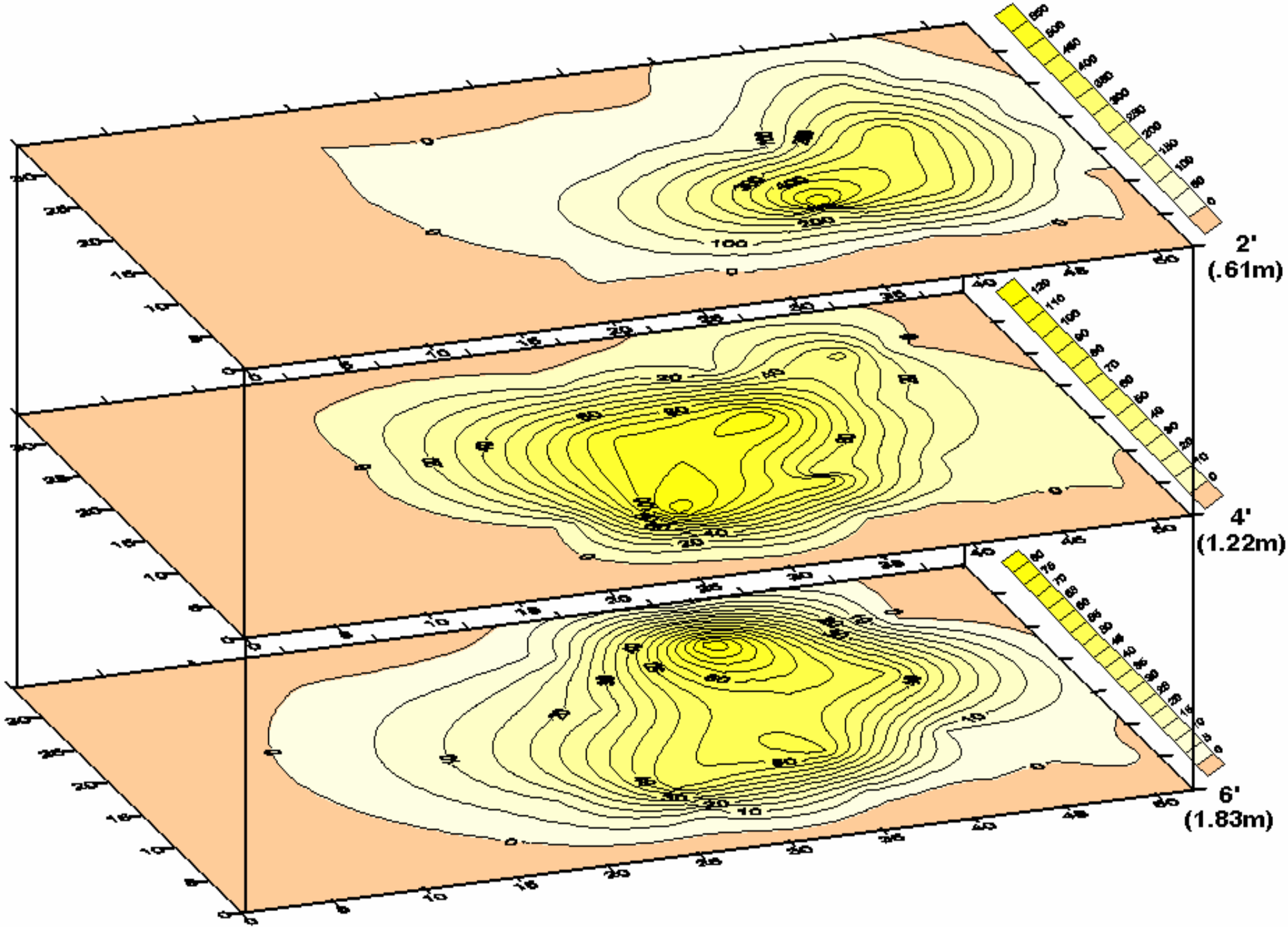
- Collected from 32 locations
- Preliminary screening by XRF
- Total chromium by ICP
- Selective extractions for Cr(VI)


±62 meters to River
Tarmac
Groundwater Flow
GP31
GP27
GP32
GP30
GP26
GP29
GP25
GP28
GP24
Break Room
13
14
10
S5
S9
S4
S8
12
9
8
S3
S7
S2
S6
S1
11
1A
1B
7
18
MW 12
Former Plating Shop
S10
15
6
2
2A
15B
19
16
5
4
3
3A
Concrete
N
2
4
6
8
10
meters
12
14
16
18
20
1997 cores
1998 cores
1999 cores

Total Chromium (Cr)



Hexavalent Chromium (CrVI)



In-Situ Redox Manipulation

Fruchter et al. (2000), Istok et al. (1999), and Amonette et al. (1994)

- **Creation of ISRM**
- **Uses chemical injection with naturally occurring Fe**
- **Creates spatially fixed reducing zone (PRB)**

Cr(VI) reduction to Cr(III) via Fe(II)/Fe(III)

- $HCrO^-_4 + 3Fe^{2+} + 7H^+ = Cr^{3+} + 3Fe^{3+} + 4H_2O$

Fe(III) Reduction By Sodium Dithonite

- $S_2O_4^{2-}(aq) + 2Fe(III)(s) + 2H_2O = 2SO_3^{2-}(aq) + 2Fe(II)(s) + 4H^+$

Reduction Studies

- sodium dithionite ($Na_2S_2O_4$)
- l-ascorbic acid ($C_6H_8O_6$)
- free hydroxylamine (FH-50™)

- **5 gm soil/25 ml reducing solution, 0.5 M**
- **Shake 24 hr, monitor Eh and pH**
- **Analyze for Cr(VI) and total metals**
- **Determine residual Cr(VI)**

Modified Bartlett and James, 1988

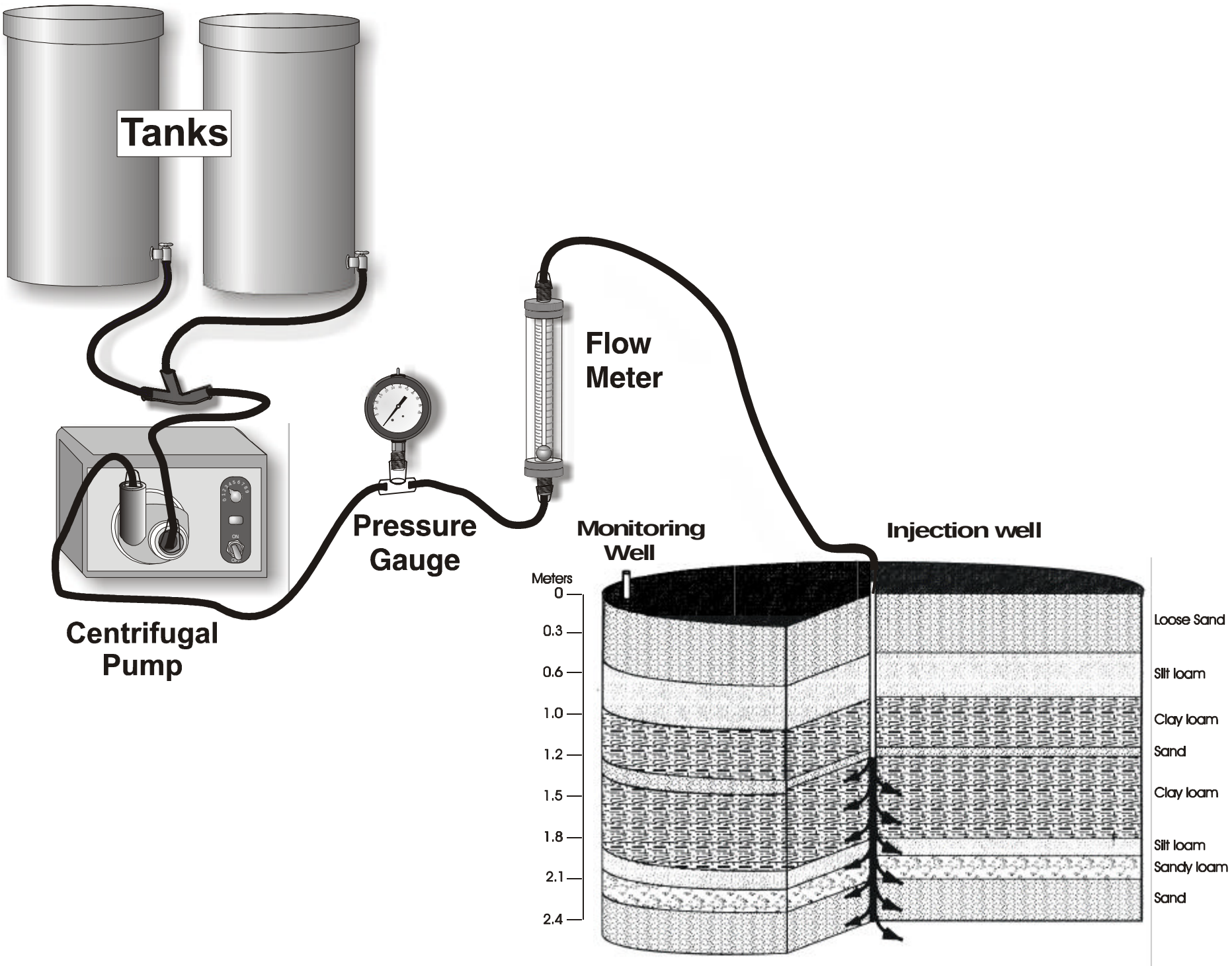
Laboratory Results

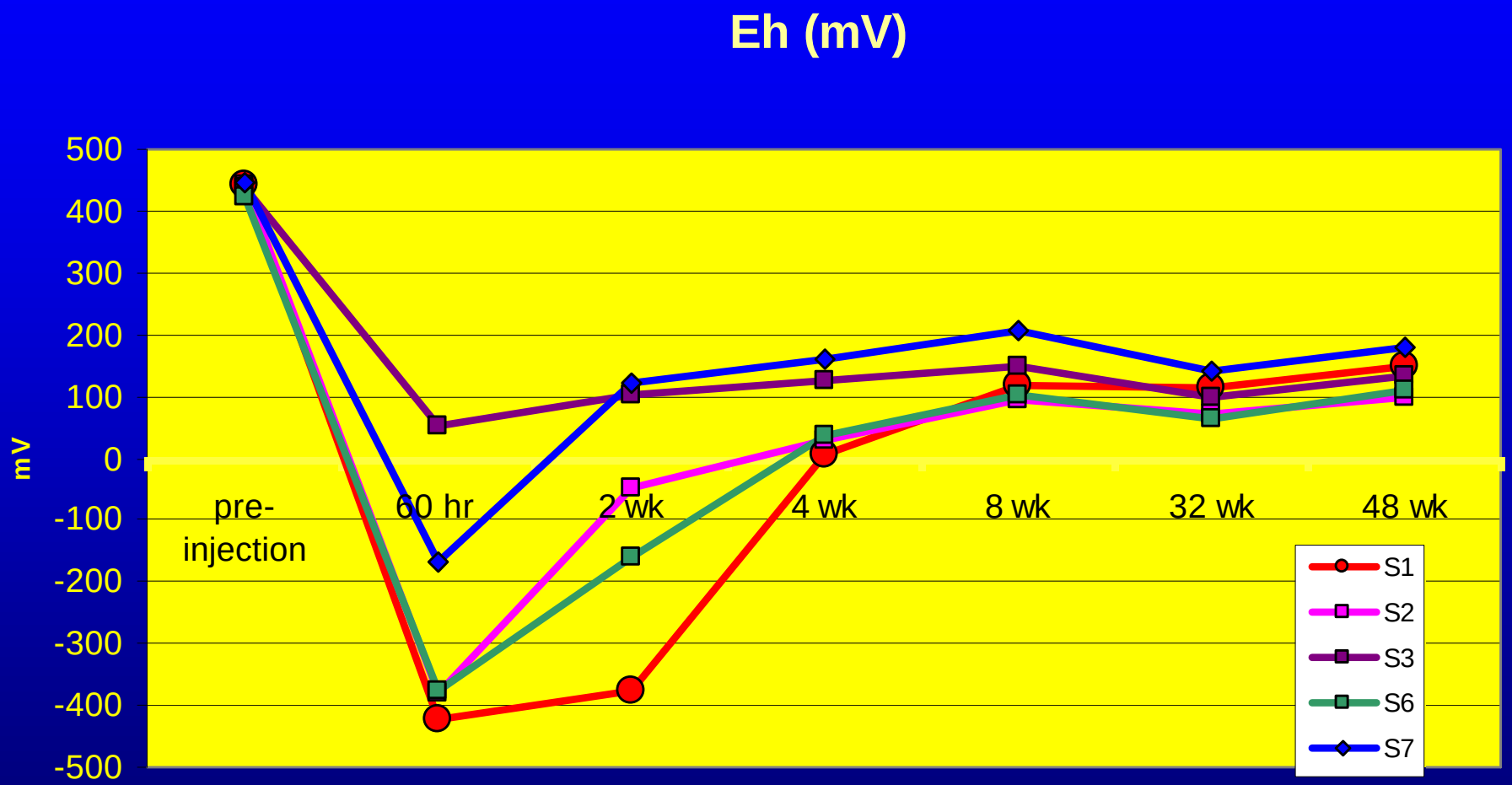
- **Eh**
  - **Sodium dithionite ~ -400 mV**
  - **Others +80 to +120 mV**
- **Fe(II) production**
  - **None detected in hydroxylamine extracts**
  - **Sodium dithionite produced significantly more**
- **Cr(VI) reduction**
  - **l-ascorbic reduced to Cr(V) and/or Cr(IV)**
  - **Sodium dithionite and hydroxylamine reduced all to Cr(III)**

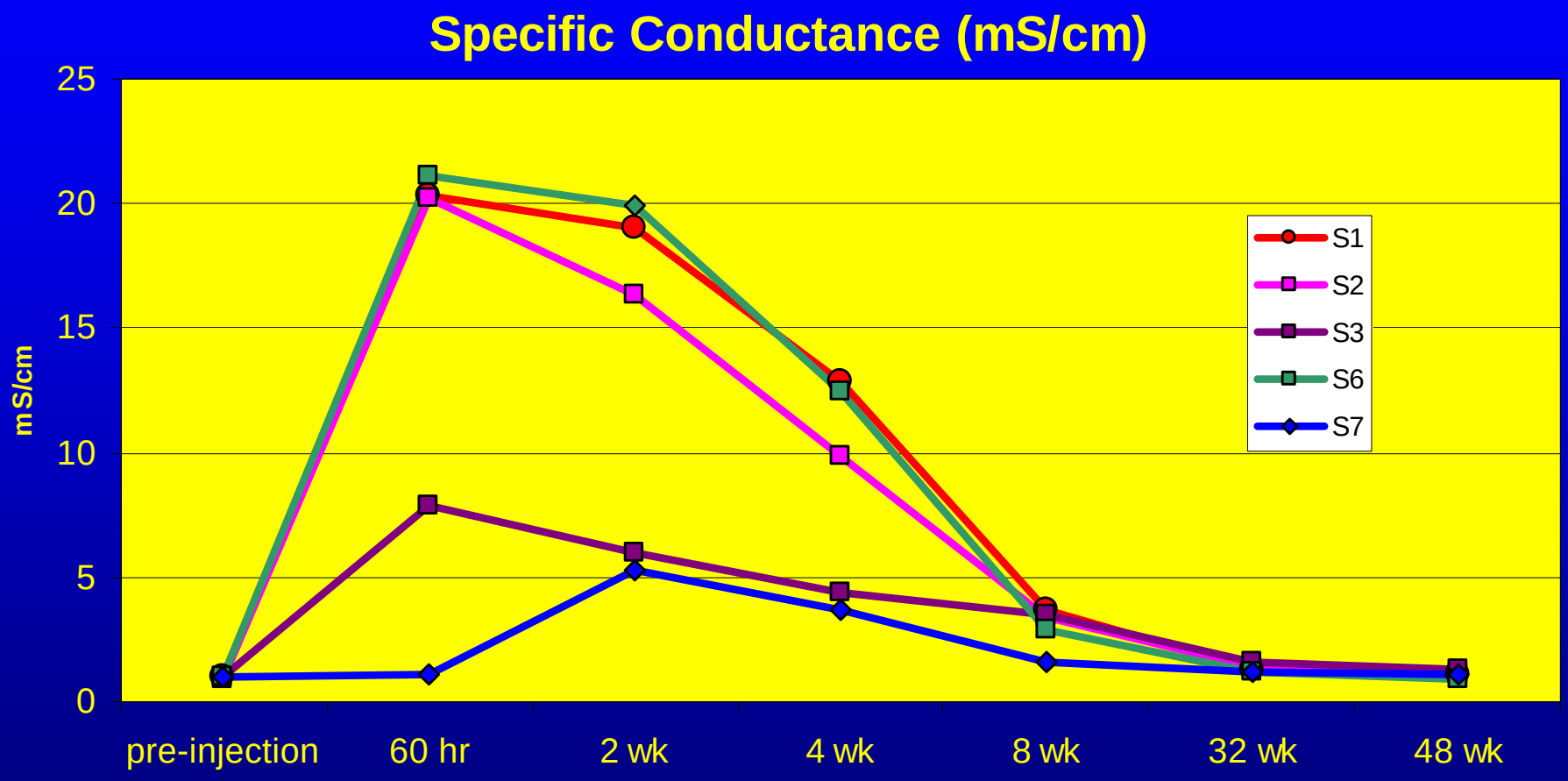
Field-Scale Pilot Study

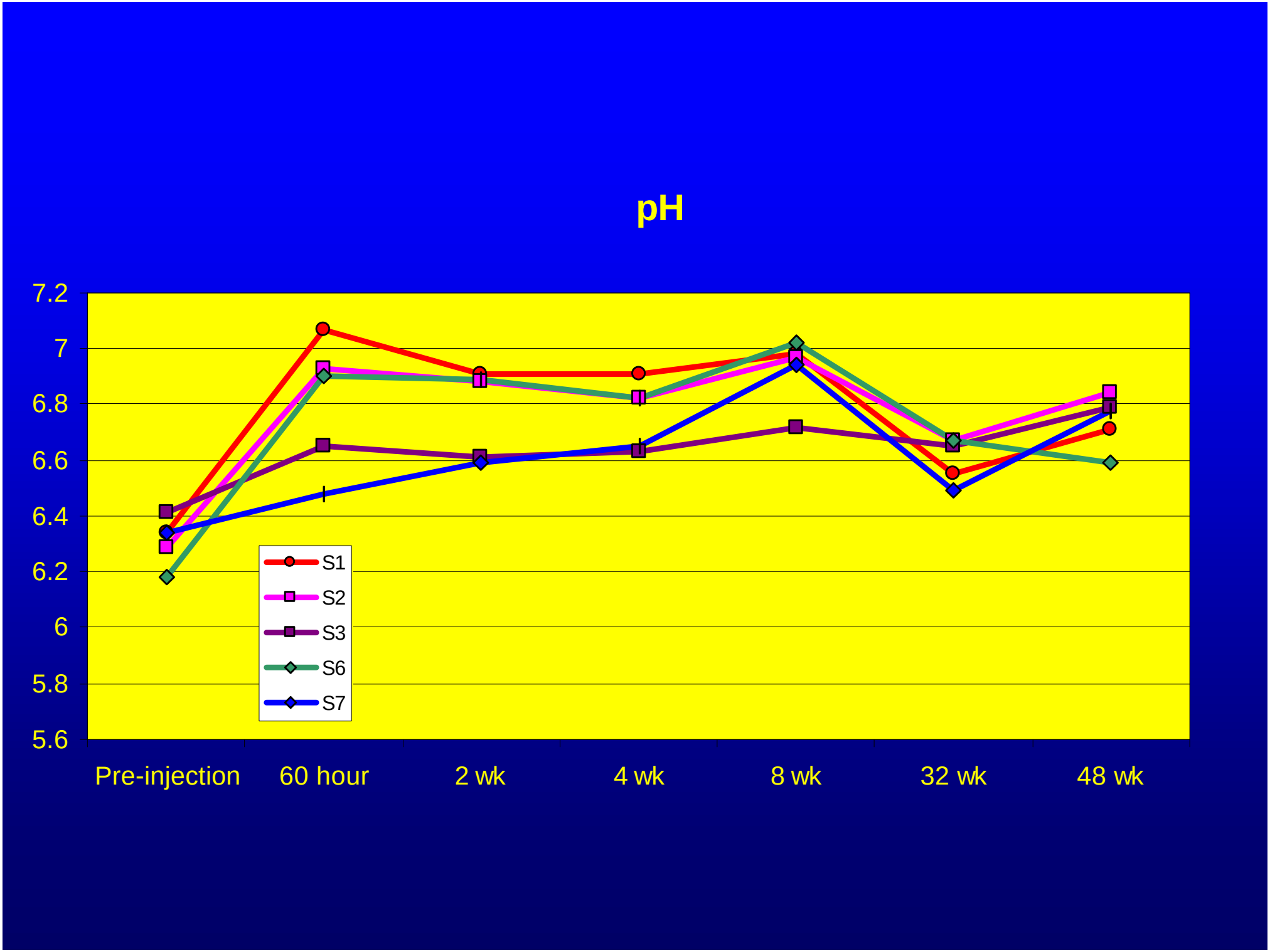
Chemical Injection

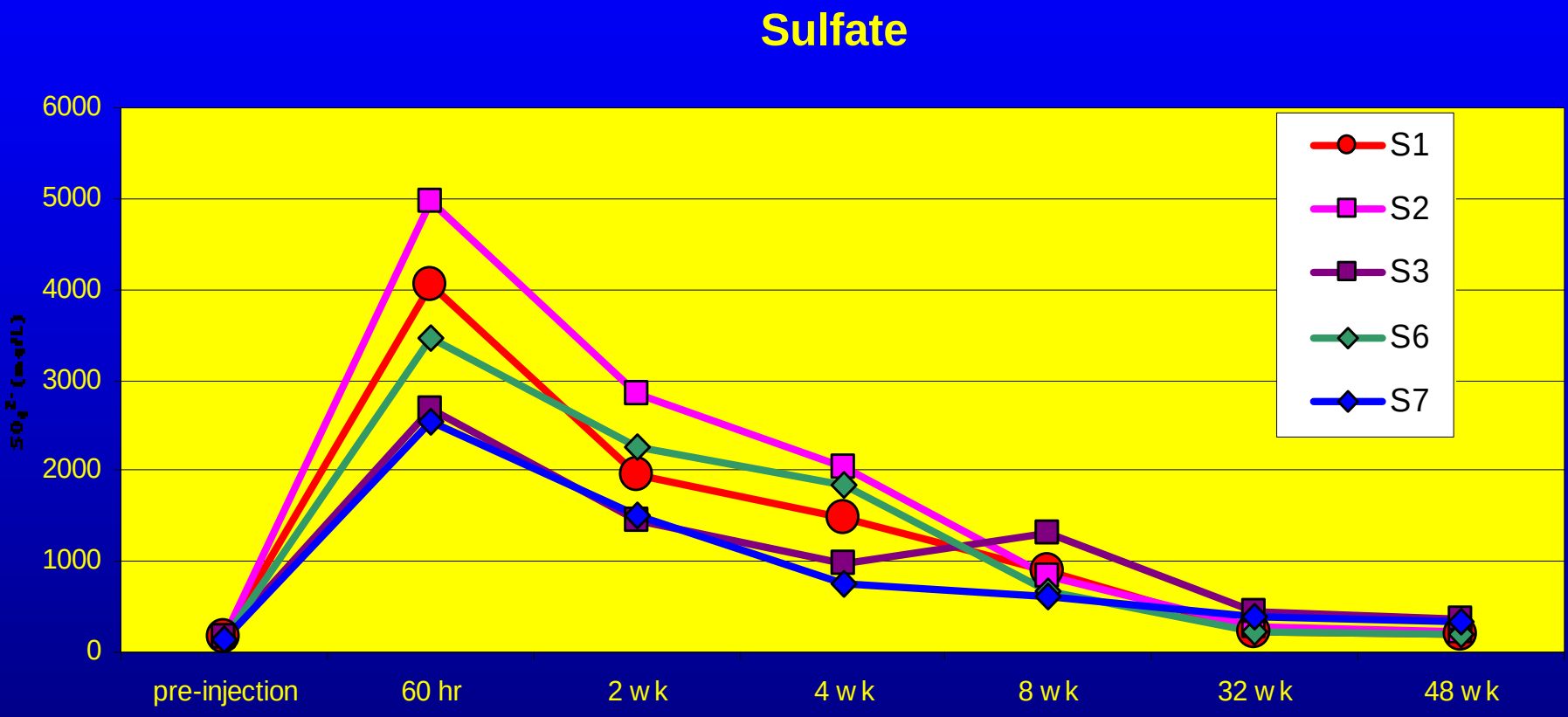
- **Distilled and deionized water = 1874 Liters (495 gallons)**
- **Sodium dithionite = 17 Kg (37.4 lbs)**
- **Potassium bicarbonate = 19 Kg (41.8 lbs)**
- **Bromide tracer = 5.63 Kg (12.4 lbs)**


Tanks
Flow Meter
Pressure Gauge
Centrifugal Pump
Monitoring Well
Injection well
Meters
0
0.3
0.6
1.0
1.2
1.5
1.8
2.1
2.4
Loose Sand
Silt loam
Clay loam
Sand
Clay loam
Silt loam
Sandy loam
Sand

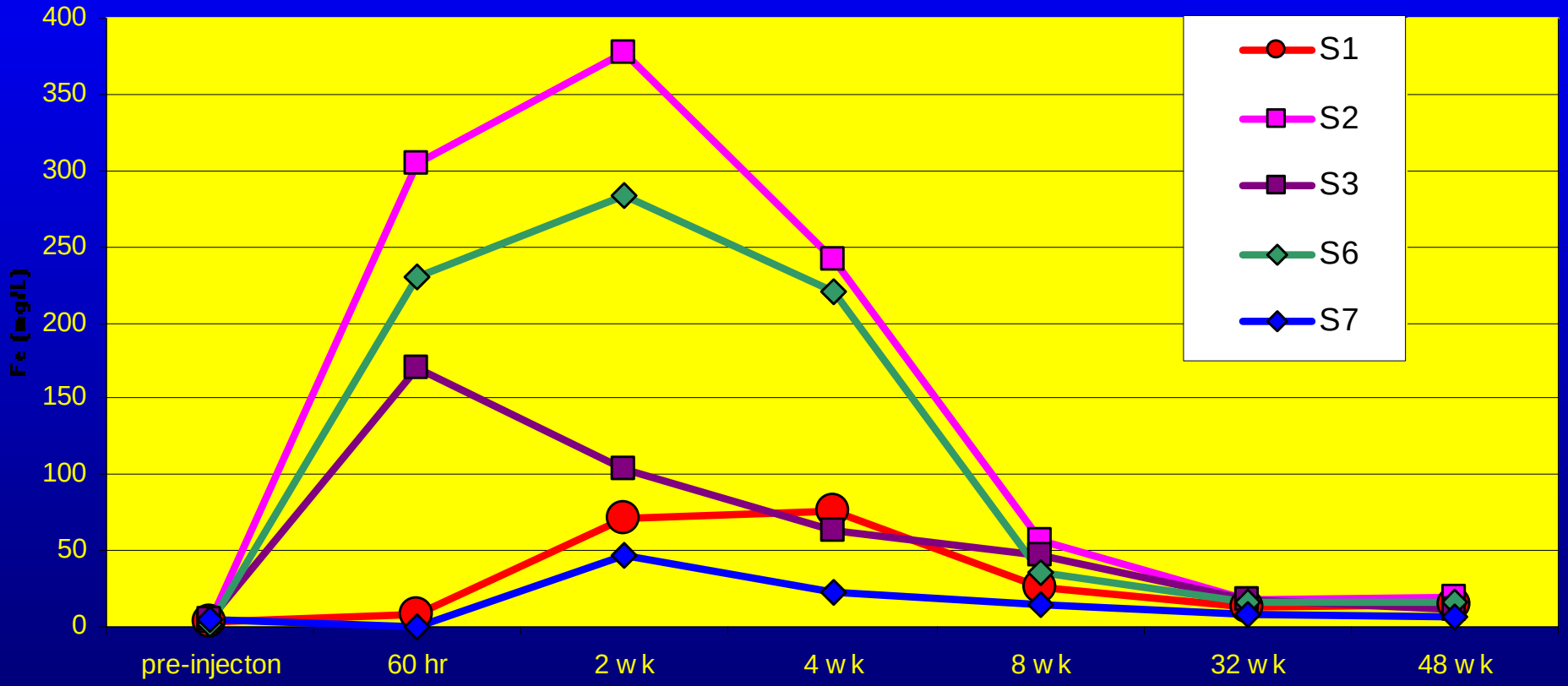

Eh (mV)
500
400
300
200
100
0
-100
-200
-300
-400
-500
mV
pre-
injection
60 hr
2 wk
4 wk
8 wk
32 wk
48 wk
S1
S2
S3
S6
S7

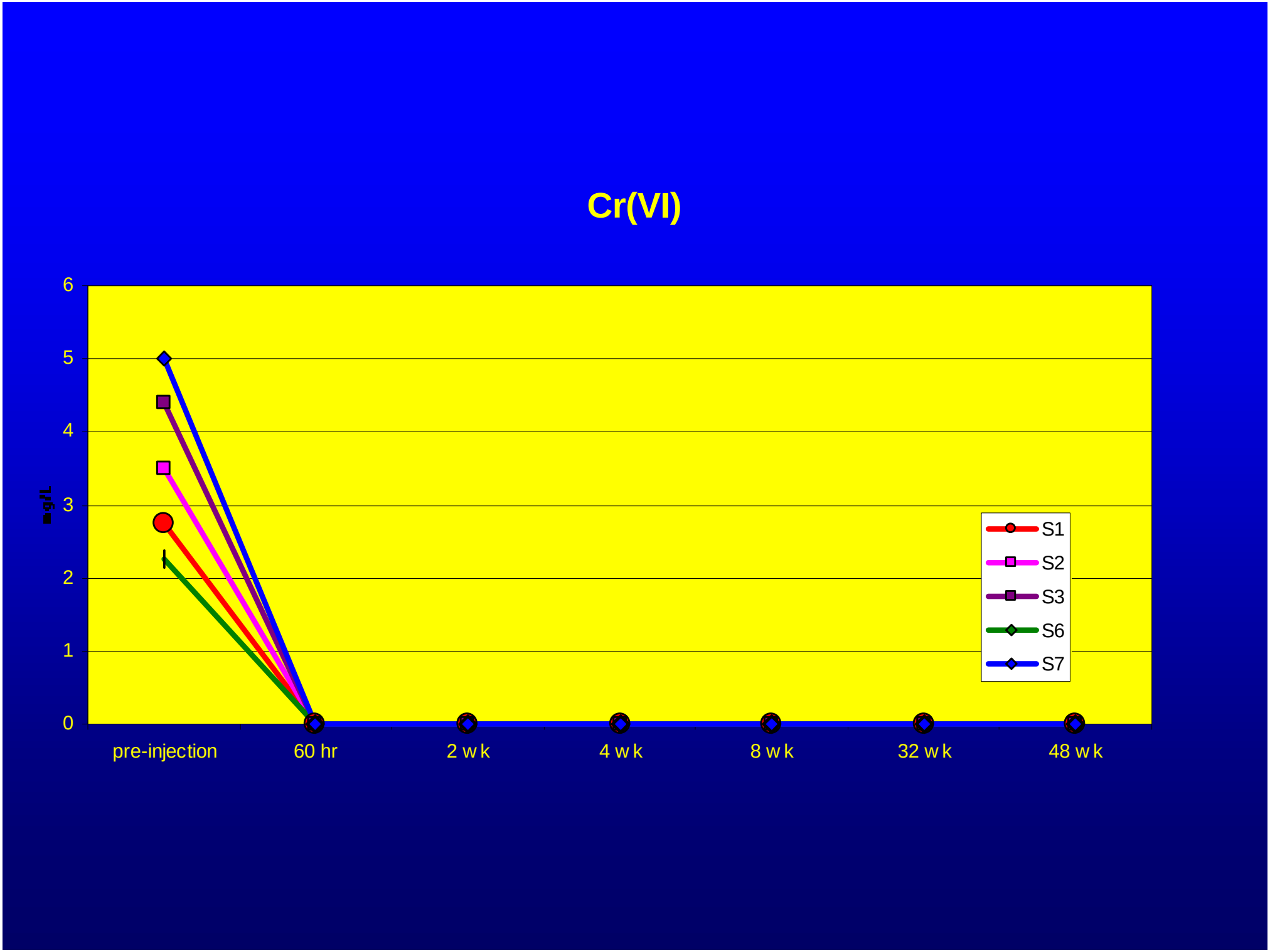

Specific Conductance (mS/cm)
mS/cm
25
20
15
10
5
0
pre-injection
60 hr
2 wk
4 wk
8 wk
32 wk
48 wk
S1
S2
S3
S6
S7


pH
7.2
7
6.8
6.6
6.4
6.2
6
5.8
5.6
S1
S2
S3
S6
S7
Pre-injection
60 hour
2 wk
4 wk
8 wk
32 wk
48 wk

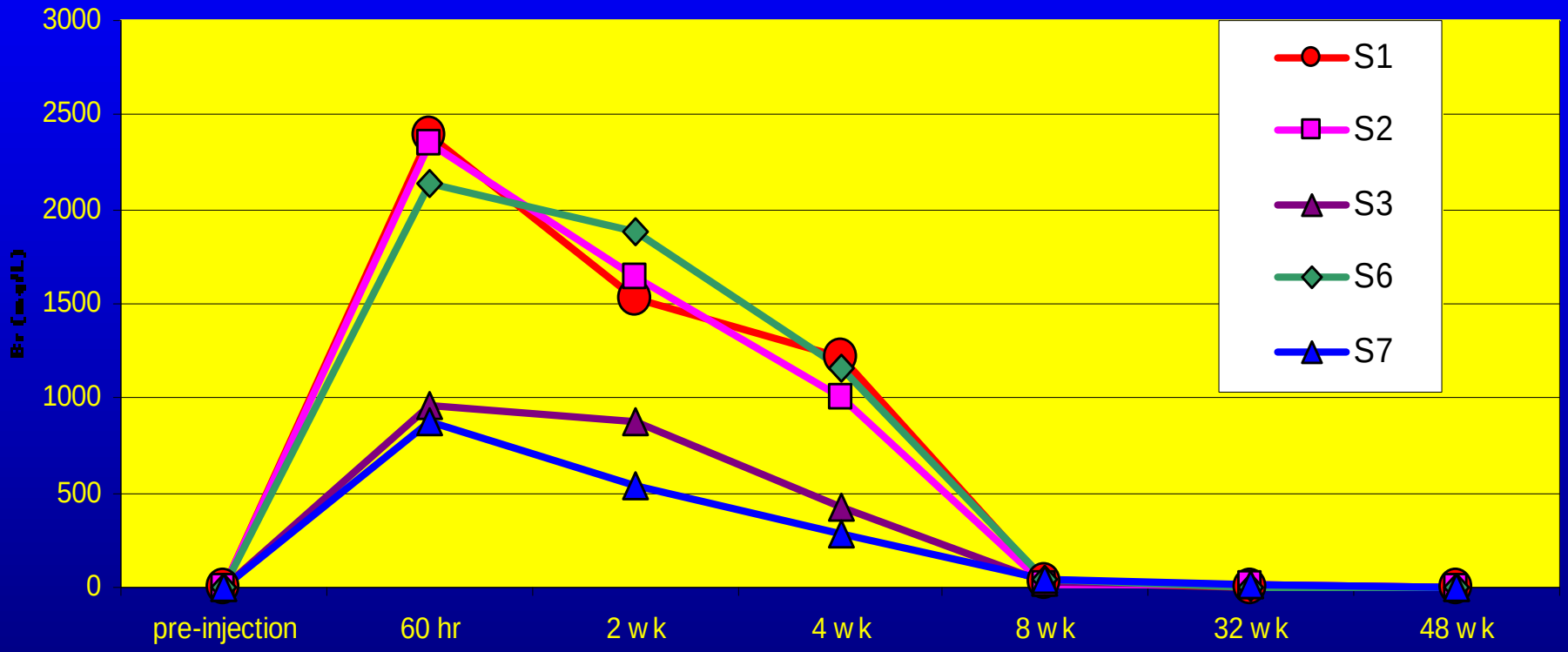

Sulfate
6000
5000
4000
3000
2000
1000
0
pre-injection
60 hr
2 wk
4 wk
8 wk
32 wk
48 wk
S1
S2
S3
S6
S7

Dissolved Iron (mg/L)

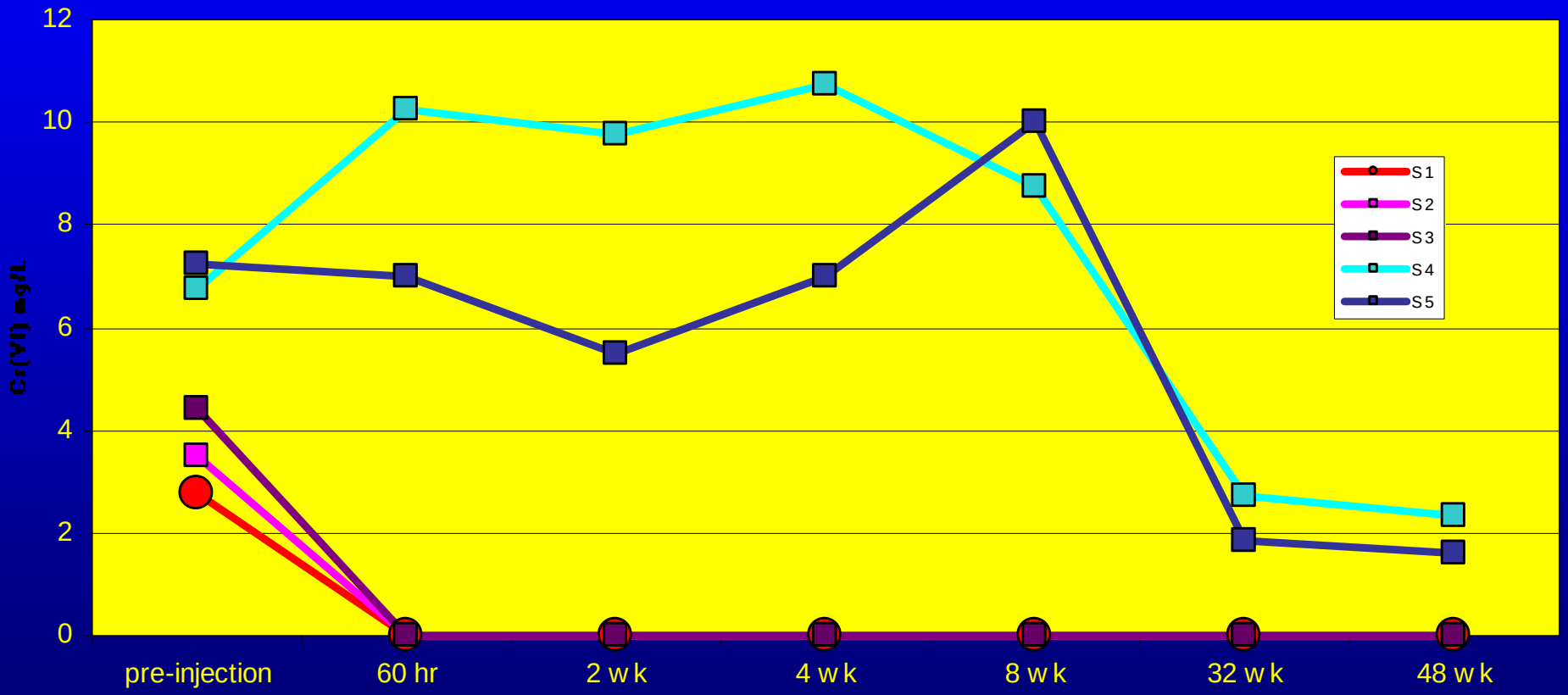


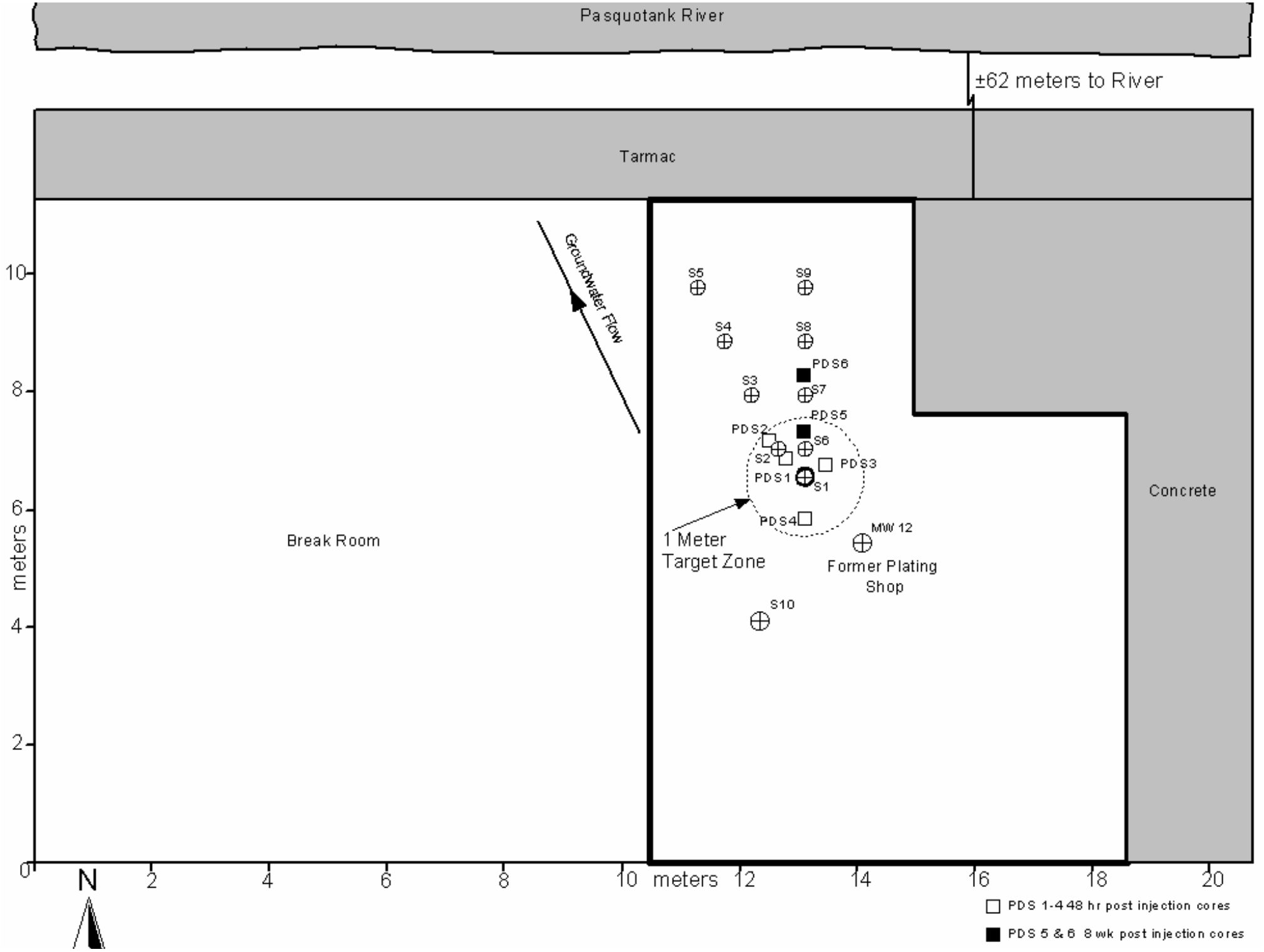

Cr(VI)
6
5
4
3
2
1
0
µg/L
pre-injection
60 hr
2 wk
4 wk
8 wk
32 wk
48 wk
S1
S2
S3
S6
S7

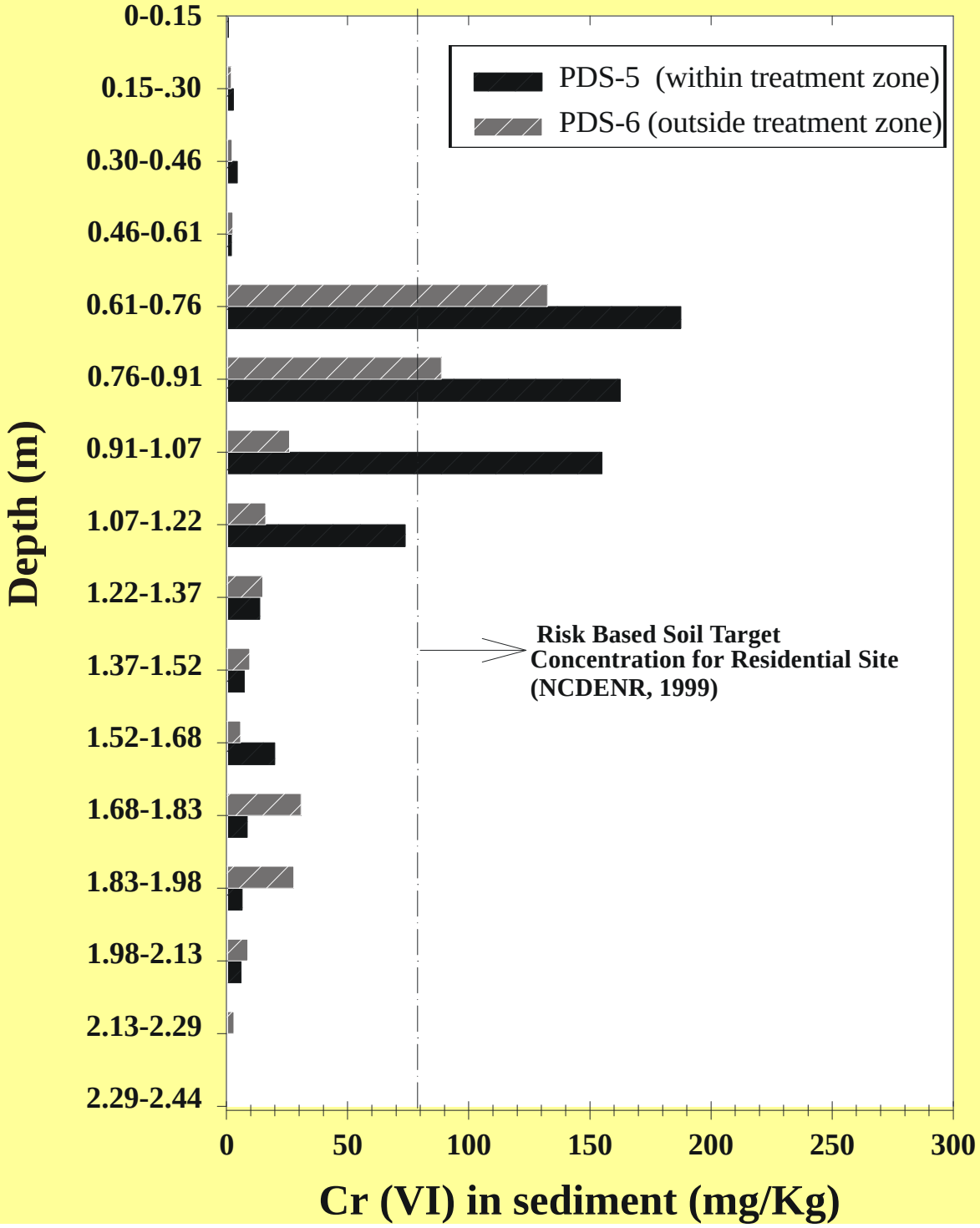
Bromide


3000
2500
2000
1500
1000
500
0
Br (mg/L)
pre-injection
60 hr
2 wk
4 wk
8 wk
32 wk
48 wk
S1
S2
S3
S6
S7

Cr(VI) in Transect 1




Pasquotank River
±62 meters to River
Tarmac
Groundwater Flow
S5
S9
S4
S8
PDS6
S3
S7
PDS5
PDS2
S6
S2
PDS3
PDS1
S1
PDS4
1 Meter
Target Zone
MW 12
Former Plating
Shop
S10
Break Room
Concrete
meters
0
2
4
6
8
10
12
14
16
18
20
N
PDS 1-4 48 hr post injection cores
PDS 5 & 6 8 wk post injection cores


0-0.15
0.15-.30
0.30-0.46
0.46-0.61
0.61-0.76
0.76-0.91
0.91-1.07
1.07-1.22
1.22-1.37
1.37-1.52
1.52-1.68
1.68-1.83
1.83-1.98
1.98-2.13
2.13-2.29
2.29-2.44
Depth (m)
PDS-5 (within treatment zone)
PDS-6 (outside treatment zone)
Risk Based Soil Target
Concentration for Residential Site
(NCDENR, 1999)
0
50
100
150
200
250
300
Cr (VI) in sediment (mg/Kg)

CONCLUSIONS

- **Sodium dithionite proved effective**
- **No adverse side effects**
- **Potential long-term reduction**

Full-Scale Implementation

- USCG selected sodium dithionite injection for full-scale remedial treatment - upper vadose zone was excavated.
- Implemented in May, 2001.
- Proven effective to date.
- May be a cost effective remedial alternative at other sites